THE EMISSION SPECTRUM OF THE CdBr MOLECULE (THE VISIBLE SYSTEM)

M. M. PATEL AND S. P. PATEL

DEPARTMENT OF PHYSICS, FACULTY OF SCIENCE

M. S. UNIVERSITY OF BARODA, BARODA, INDIA

(*Received July* 8, 1965; *Resubmitted May* 10, 1966)

ABSTRACT. The spectrum of CdBr was reinvestigated in emission using a high frequency discharge from a 125 Watt oscillator working in the frequency range 10 to 15 M.c/sec. A system of bands degraded to red, designated as $B^2\Sigma \rightarrow X^2\Sigma$ and occuring in the region λλ4900-3900 has been photographed with Hilger medium quartz and E_2 glass spectrographs. In addition to the bands already observed by various investigators, a number of new bands have been recorded in the present investigation. The existance of isotopice effect of Br^{79} and Br^{81} is established for about ten bands. The vibrational analysis of the band system is given and the following vibrational quantum formula is derived.

$$\nu_{head} = 24822.6 + [105.4(v' + \tfrac{1}{2}) - 1.70(v' + \tfrac{1}{2})^2] - [229.9(v'' + \tfrac{1}{2}) - 0.47(v'' + \tfrac{1}{2})^2]$$

INTRODUCTION

The spectra of halides of zinc, cadmium and mercury have been investigated in various degrees of detail by different workers. [Wieland (1929, 1941), Oeser (1935), Ramasastry and Rao (1946), Ramasastry (1947), Ramasastry and Sreeramurthy (1950)]. These molecules show systems of two general types. One type is a short wavelength range system on the longer wavelength side of Zn, Cd or Hg lines in the ultraviolet region. The other type is a group of crowded bands, degraded to red, on a continuum with pronounced intensity maxima in the red region. In the short wavelength region of the visible spectrum, however, progression type of bands with a partial resolution into rotational lines are observed in a number of these molecules.

Two previous investigations have been made on the spectrum of CdBr. Wieland (1929) obtained the vibrational spectrum of this molecule in a high-frequency discharge in the region 3250–3120Å, consisting of violet degraded bands. Howell (1943) suggested that these bands form one of the components of the $^2\Pi \rightarrow {}^2\Sigma$ transition but could not succeed in observing the other one. Ramasastry (1949) obtained some additional bands and atrributed these to the missing component of the Wieland system. Wieland (1929) also mentioned the occurrance of the diffuse bands extending from 6400 to 3300Å. Using a high-frequency source, later, Ramasastry (1949) obtained these visible bands extending from 4900–3850Å. Measurements of about fifty bands were reported and a regularity of intervals was indicated which was of the order of about 110 cm^{-1}.

In continuation of our work on the spectrum of CdCl (1966), a reinvestigation of the bands of CdBr in this region was also undertaken and the results obtained are reported here.

EXPERIMENTAL

The spectrum of cadmium bromide was excited in a high frequency discharge from a 125 Watt oscillator working in the frequency range 10—15 Mc/sec. A pure sample of the substance was kept in a small quartz boat at the centre of a straight tube of quartz of about 25 cm. in length and 1.5 cm. in diameter. The discharge was established by external electrodes and was maintained bright-white in colour by strong heating. Continuous evacuation of the discharge tube with a high vacuum pump was necessary. Photographs of the spectra in the visible region were taken with the Hilger medium quartz spectrograph and with Hilger E_2 glass spectrograph, the latter having a dispersion of about 16 Å/mm. at 4300Å. An exposure of about 20 to 30 minutes was found adequate to record the spectrum with Ilford process plates. Iron arc lines were used as standards for determining the wavelengths. The wavelengths of the band heads reported here are averages of several independent settings of different plates.

RESULTS

The spectrum of cadmium bromide bands is reproduced in figs. 1 and 2. The bands are degraded towards the red. The bands on the longer wavelength side have sharp edges getting diffuse and broad towards shorter wavelength. Some of the bands in the region 4800-4400Å show sharp double heads. In table I the wavelengths, wave numbers in vacuum and visually estimated values of intensities of the bands obtained in the present investigation are given. In the fifth column the wave numbers of the bands reported by Ramasastry (1949) are given for comparison. The classification of bands is given in column 4. The calculated values along with observed isotopic shifts for about ten bands have been given in table II.

DISCUSSION

In addition to forty nine bands already reported by Ramasastry (1949), nearly ninety bands have been observed and measured in the present investigation. When the most intense bands taken alternately are arranged in a row, the wave number intervals show a regular decrease for about three groups of bands. Hence they are considered as members of a progression of the lower state of this molecule. When the bands in this region were assigned to three different v'-progressions, it was possible to get the lower state difference of about 230 cm^{-1}. Following the standard procedure (Herzberg, 1950) for calculating the vibrational constants, the band head equation given below, was derived, and this accounts in a satis-

Indian Journal of Physics Vol 41 No. 3
PLATE - I A

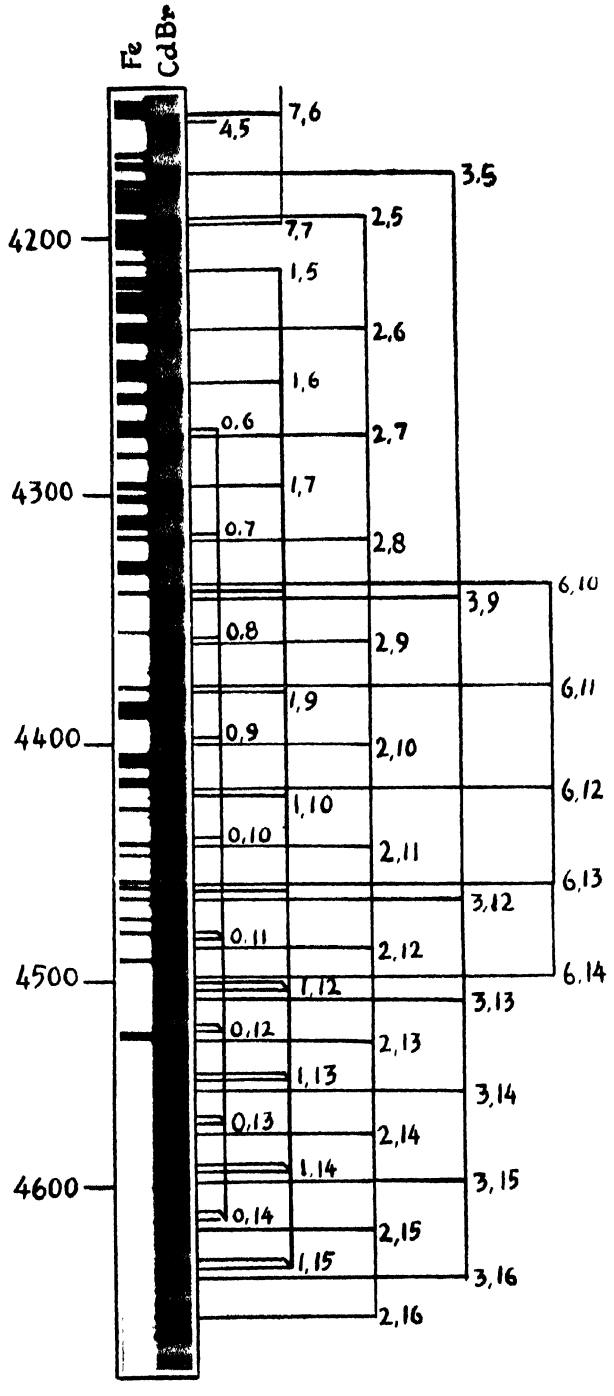

Fig 1. CdBr bands taken with a E_2^* glass spectrograph

Indian Journal & Physics Vol. 41 No. 3

PLATE-1B.

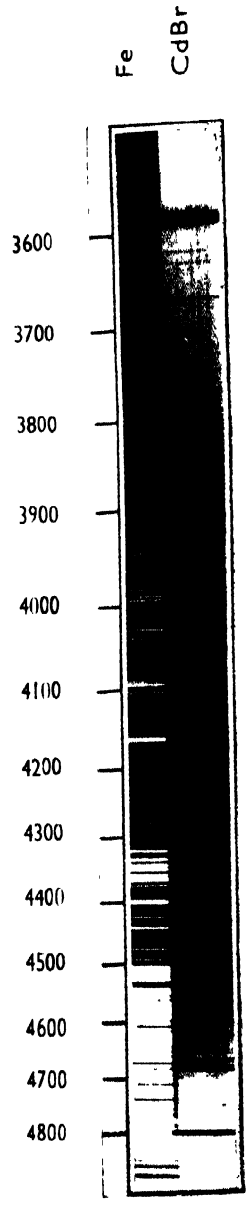

Fig 2. CdBr bands taken with low dispersion spectrograph

factory manner for all the observed bands. The agreement of ν_{obs} and ν_{cal} is shown is Column 6, table 1.

$$\nu_{head} = 24822.6+[105.4(v'+\tfrac{1}{2})-1.70(v'+\tfrac{1}{2})^2] -[229.9(v''+\tfrac{1}{2})-0.47(v''+\tfrac{1}{2})^2].$$

When the bands are arranged in a Deslandres table, the intensity distribution bears a close resemblance to that observed in the corresponding systems of the halides of zinc and mercury. The Condon parabola for the system appears to be sufficiently wide which probably accounts for the poor intensities of the bands having lower v' and v'' values.

As the two isotopes of bromine (Br^{79} and Br^{81}) occur in the ratio of 50.57 : 49.43 one may expect the intensities of the corresponding isotopic bands to be nearly the same. In the region 4700 to 4400 Å this isotope effect gives the bands a double headed appearance. The isotopic shift for the band (v', v'') is given by

$$\nu_{v_i} - \nu_v = \Delta\nu = (\rho-1)[\omega'_e(v'+\tfrac{1}{2})-\omega_e''(v''+\tfrac{1}{2})] -(\rho^2-1)[\omega'_e x'_e(v'+\tfrac{1}{2})^2-\omega''_e x''_e(v''+\tfrac{1}{2})^2]$$

where ν_{v_i} refers to $CdBr^{81}$ and ν_v to $CdBr^{79}$. The isotopic factors $(\rho-1)$ and (ρ^2-1) come out to be -0.00723 and -0.01443 respectively. Using these values the isotopic shifts for about ten bands were calculated. The observed separations were then compared with the calculated values. The agreement is quite close and is shown in Table II.

If the molecule cadmium bormide is formed from cadmium and bromine atoms, both taken in their normal states, the possible electronic states are $^2\Sigma^+$ and $^2\Pi$

$$^1S(Cd)+{}^2P(Br)\rightarrow {}^2\Sigma^+ \text{ and } {}^2\Pi(CdBr).$$

As the lowest electronic states of a molecule are usually those that dissociate into their normal atoms, these $^2\Sigma^+$ and $^2\Pi$ states may be taken as the low levels of cadmium bromide molecule. These two states represented in the usual notation can be expressed as

$$\sigma^2\sigma^2\pi^4\sigma,\ {}^2\Sigma^+$$
$$\sigma^2\sigma^2\pi^3\sigma^2,\ {}^2\Pi_i$$

The inverted $^2\Pi$ state will be one of the low lying states and may be nearer to $^2\Sigma^+$ state. A band system expected due to the transition $\sigma^2\sigma^2\pi^3\sigma^2,\ {}^2\Pi_i \rightarrow \sigma^2\sigma^2\pi^4\sigma,\ {}^2\Sigma^+$ should be of very low energy and may appear in the infra-red region, or the non-appearence of the above transition may be due to the fact that $^2\Pi_i$ may be a repulsive state.

The system B lying in the region 3900–4900 Å consists of red degraded bands. As most of the bands excepting those in the region 4400-4700 Å are single headed and that these double headed bands are due to isotope effect the transition may

TABLE I

Band heads of CdBr in the region 4900 to 3900Å

Intensity	Wavelength	Observed Wave Number in vacuum	v', v''	Value observed by Ramasastry	$\nu_{obs} - \nu_{cal}$ in cm^{-1}
2	4908.53	20367	0, 20	—	−1
1	4884.55	20467	1, 20	—	−3
1	4867.19	20540	4, 21	—	−5
1	4861.28	20565	2, 20	—	−3
2	4834.24	20680	1, 19	20691	0
2	4808.43	20791	0, 18	20793	+1
3	4785.65	20890	1, 18	20905	−2
1	4768.52	20965	4, 19	—	−1
2	4762.62	20990	2, 18	—	−1
3	4759.67	21004	0, 17	21014	+1
3	4734.98	21118	—	21120	—
1	4729.05	21140	6, 19	—	+4
2	4720.79	21177	4, 18	—	−1
3	4714.78	21204	2, 17(79)	21215	+1
2	4709.03	21230	2, 17(81)	—	—
1	4700.81	21267	5, 18	—	+1
2	4693.75	21299	3, 17(79)	—	+1
2	4688.02	21325	3, 17(81)	21319	—
4	4668.10	21416	2, 16(79)	—	−1
3	4662.88	21440	2, 16(81)	21444	—
3	4647.70	21510	3, 16	—	−2
4	4642.74	21533	1, 15(79)	21531	0
4	4638.04	21555	1, 15(81)	21555	—
4	4631.77	21584	9, 18	—	−2
5	4622.13	21629	2, 15	—	−2
4	4618.72	21645	0, 14(79)	21644	−1
4	4614.03	21667	0, 14(81)	21668	—
4	4608.92	21691	5, 16	—	−1
5	4601.71	21725	3, 15	—	−1
5	4597.26	21746	1, 14(79)	—	−2

TABLE I (*contd.*)

Intensity	Wavelength	Observed Wave Number in vacuum	v', v''	Value observed by Ramasastry	$\nu_{obs} - \nu_{cal}$ in cm^{-1}
4	4592.62	21768	1, 14(81)	21758	—
3	4586.93	21795	9, 17	—	−3
6	4576.63	21844	2, 14	—	−3
6	4573.29	21860	0, 13(79)	—	−2
5	4568.92	21881	0, 13(81)	21874	—
3	4563.89	21905	5, 15	—	−2
6	4556.40	21941	3, 14	—	−1
7	4551.43	21965	1, 13(79)	—	+1
6	4547.49	21984	1, 13(81)	21979	—
4	4542.12	22010	9, 16	—	−2
7	4531.83	22060	2, 13	—	−3
8	4528.13	22078	0, 12(79)	—	−2
7	4524.44	22096	0, 12(81)	22090	—
4	4519.32	22121	5, 14	—	−1
8	4512.19	22156	3, 13	—	−2
9	4507.30	22180	1, 12(79)	—	−2
9	4503.85	22197	1, 12(81)	22194	—
3	4501.83	22207	6, 14	—	0
4	4495.95	22236	—	—	—
9	4487.68	22277	2, 12	—	−3
9	4484.06	22295	0, 11(79)	22295	−3
9	4480.84	22311	0, 11(81)	—	—
9	4468.42	22373	3, 12	—	−2
9	4463.04	22400	1,11	22407	0
4	4459.06	22420	6, 13	—	−3
9	4444.19	22495	2, 11	—	−3
10	4440.63	22513	0, 10(79)	22522	−4
9	4437.68	22528	0,10(81)	—	—
3	4432.95	22552	5, 12	—	−4
10	4420.41	22616	1, 10	—	−3

TABLE I (*contd.*)

Intensity	Wavelength	Observed Wave Number in vacuum	v', v''	Value observed by Ramasastry	$\nu_{obs} - \nu_{cal}$ in cm^{-1}
8	4416.30	22637	6, 12	—	−4
9	4400.95	22716	2, 10	—	−2
8	4397.27	22735	0, 9	22731	−2
9	4377.63	22837	1, 9	22844	−2
7	4374.38	22854	6, 11	—	−5
8	4359.50	22932	2, 9	—	−3
7	4354.94	22956	0, 8	22954	−2
8	4340.57	23032	3, 9	—	−1
8	4335.68	23058	1, 8	23057	−2
4	4332.85	23073	6, 10	—	−5
8	4317.51	23155	2, 8	—	−4
7	4313.42	23177	0, 7	23168 23213 (Chlorine atomic-line)	−3
7	4294.51	23279	1, 7	23278	−3
7	4276.33	23378	2, 7	—	−3
3	4272.30	23400	0, 6	23390	−3
6	4253.58	23503	1, 6	23496	−2
6	4235.99	23601	2, 6	23609	−3
7	4218.76	23697	3, 6	—	−2
3	4213.60	23726	1, 5	23723	−3
5	4197.32	23818	7, 7	—	−5
4	4196.27	23824	2, 5	23826	−3
5	4179.08	23922	3, 5	—	0
4	4175.76	23941	—	23942	—
4	4163.24	24013	4, 5	—	−1
3	4158.40	24041	7, 6	24039	−5
3	4140.31	24146	3, 4	24149	−1
2	4120.68	24261	10, 6	24267	−9
3	4105.96	24348	8, 5	24364	0
+3	4086.66	24463	4, 3	24469	−3

TABLE I (*contd.*)

Intensity	Wavelength	Observed Wave Number in vacuum	v', v''	Value observed by Ramasastry	$\nu_{obs} - \nu_{cal}$ in cm^{-1}
+2	4068.53	24572	8, 4	24580	0
+2	4049.08	24690	4, 2	24694	−2
+2	4031.77	24796	8, 3	24803	−2
+2	4012.52	24915	4, 1	24908	−4
+2	3997.75	25007	5, 1	25010	−1
+2	3978.82	25126	13,3	25129	—
+1	3961.48	25236	5, 0	25230	0
+1	3943.20	25352	13, 2	25346	—
+1	3927.08	25457	11, 1	25448	—
+0	3917.10	25522	12, 1	—	—

+Measurements made on the plate taken with a medium quartz Spectrograph.

TABLE II

Assignment v', v''	Observed shift in cm^{-1}	Calculated shift in cm^{-1}
0, 10	15	15
0, 11	16	17
0, 12	18	19
0, 13	21	20
0, 14	22	22
1, 12	17	18
1, 13	19	19
1, 14	22	21
1, 15	22	23
2, 16	24	24
2, 17	26	25
3, 17	26	25

Fig. 1. CdBr bands taken with a E_2 glass spectrograph.

Fig. 2. CdBr bands taken with low dispersion spectrograph.

in all probability be $^2\Sigma^+ \rightarrow {}^2\Sigma^+$. The electron configuration $\sigma^2\sigma\pi^4\sigma^2$ gives rise to $^2\Sigma^+$ state which will also be one of low energy. The upper state of the visible bands may hence be identified with this state. The change of an electron from an inner σ to an outer σ orbit is consistent with the expected decrease in the vibrational frequency of the red degraded band system. This $^2\Sigma^+$ and the other excited states of the molecule will be those which could be derived from cadmium and bromine atoms, with one, or the other, or both of them, in their excited atomic states. If the cadmium atom is taken in the first excited state and the bromine atom is taken in the normal state it gives rise to $\Sigma^+(2)$, Σ^-, $\Pi(2)$ and Δ doublet and quartet states. The doublet levels alone should be considered here. Selection rules do not permit the levels $^2\Sigma^-$ and $^2\Delta$ to combine with the ground state. A $^2\Sigma^+ \rightarrow {}^2\Sigma^+$ transition in this region is therefore expected.

A group of bands in the region 5000 to 6400 Å have also been recorded in the present investigation. They are degraded to red but are diffuse in appearance. Attempts are being made to analyse them.

ACKNOWLEDGMENTS

The authors wish to express their thanks to Prof. N. S. Pandya for his keen interest in this work. One of the authors (S.P.P.) is grateful to the Council of Scientific and Industrial Research, New Delhi, for the award of a Research Fellowship.

REFERENCES

Herzberg, G., 1950, *Spectra of Diatomic Molecules*, D. Van Nostrand Co., Inc., New York.
Howell, H. G., 1943, *Proc. Roy. Soc., A* **182**, 95.
Patel M. M., and Patel S. P., 1966, *Indian J. Pure. Appl. Phys.* **4**, 388,
Oeser, E., 1935, *Z. P.*, **95**, 699.
Ramasastry, C., and Rao, K. R., 1946, *Indian J. Phys.*, **20**, 100.
Ramasastry, C., 1947, *Indian J. Phys.*, **21**, 265.
Ramasastry, C., and Sreeramurthy K., 1950, *Proc. Nat. Inst. Sci.*, Indian, **16**, 305.
Ramasastry, C., 1949, *Indian J. Phys.*, **23**, 453.
Wieland, K., 1929, *Helv. Phys. Acta.*, **2**, 46 and 77.
————, 1941, *Helv. Phys. Acta.*, **14**, 420.